

S1. Atlantic Ocean Acidification Test-bed (AOAT)

The test-bed project was only a five (5) year project. Since then the time-series has been designated as a National Coral Reef Monitoring Program (NCRMP) Climate Station. It also represents an important contributing node to the National Ocean Acidification Observing Network (NOA-ON) advanced by NOAA's Pacific Marine Environmental Laboratory (PMEL, www.pmel.noaa.gov/co2). The NOA-ON designation refers to the autonomous buoy along with the discrete carbonate chemistry monitoring. The addition of the ancillary ecological measures (e.g. calcification, bio-erosion, temperature) make it into a NCRMP Climate Station.

This joint effort by NOAA, the University of Miami/RSMAS (Rosenstiel School of Marine and Atmospheric Science), the University of Puerto Rico, Mayagüez Campus (UPRM) and the Caribbean Coastal Ocean Observing System (CARICOOS) program has sought to serve as a nexus of federal and academic monitoring and research related to assessing the impacts of OA on Caribbean coral reef ecosystems.

S2. *In situ* geochemical surveys Collection and Analyses

The *in situ* geochemical surveys included profile measurements of chemical and physical parameters using a SBE25® conductivity, temperature, and depth recorder (CTD), and bottle water samples for TA and pH at the buoy site. Seawater samples were collected using a Van Dorn type sampler bottle at approximately 2-3 m depth. The seawater samples were drawn from the sampler into 250 mL Biological Oxygen Demand (BOD) flasks and stored at room temperature for rapid analysis at the nearby UPRM marine station (Fig.2). If TA and pH analyses were not accomplished within 24 hr of sampling, each sample is poisoned with a saturated solution of mercuric chloride (HgCl₂; 100 µl) to prevent biological alteration (Dickson et al., 2007). Each bottle was sealed tightly to prevent atmospheric gas exchange.

The pH samples were analyzed in triplicate on a UV-VIS spectrophotometer with purified m-cresol purple as an indicator (Clayton and Byrne, 1993) according to the DOE procedures (DOE, 1994) with implemented precision of ± 0.01. Each sample was analyzed in triplicate in 10 cm path length quartz cylindrical cells with deionized water in the background over a wavelength range to 425 to 790 nm in 1.0 nm intervals. The TA seawater analyses were measured with a precision of ±2-3 µmol kg⁻¹ by Gran titration (Gran, 1952) using Dickson Certified Reference Materials (CRMs) to standardize the nominal 0.1 N hydrochloric acid (HCl) titrant (for details of the CRMs see Dickson et al., (2003)). Temperature of the samples were held constant at 25°C using a water bath.

S3. Ocean end-member - Caribbean Cruises

In situ TA and DIC samples from seasonal cruises around the Caribbean Region, including three cruises to the Caribbean Time Series station (CaTS) on 2011 and 2012. The cruises include data from the A22 CLIVAR and WOCE transect, the Global Ocean Data Analysis Project, the Carbon Dioxide in the Atlantic Ocean (CARINA), and other cruises around the area in different years from 1997 to 2008. Measurements were selected for the first 100 m depth and for SST higher or equal to 25°C.

S4. Constructing an annual climatology - Data Gaps

Data gaps on $p\text{CO}_{2,\text{sw}}$, $p\text{CO}_{2,\text{air}}$, SST, and SSS buoy measurements occurred intermittently in 2010, 2012, 2014, and 2017 (<50 %) due to instrument failure. The SST and SSS gaps from 2010 were filled with the nearby ICON buoy measurements. The SST and SSS gaps from 2014 and 2017 were filled in with the seasonal averages. Average difference between SST and SSS measurements from the ICON and the MapCO₂ buoys were <0.05°C and <0.0008, respectively. The gaps in $p\text{CO}_{2,\text{sw}}$ and $p\text{CO}_{2,\text{air}}$ were filled in with the with the average daily observations from 2009 to 2017.

S5. Error Analyses

Published uncertainty from the Sea-Bird Electronics (SBE16/37) for temperature and salinity and the laboratory-based accuracy of TA and pH were used. The uncertainty on the gas exchange was estimated using the propagation of errors method. This includes the uncertainties associated with the buoy $p\text{CO}_{2,\text{sw}}$, $p\text{CO}_{2,\text{air}}$, and O₂ observations; the gas transfer velocity uncertainty (Wanninkhof, 2014); and the relative standard error associated with the data-fill using the climatological curve created with the two wind speed datasets.

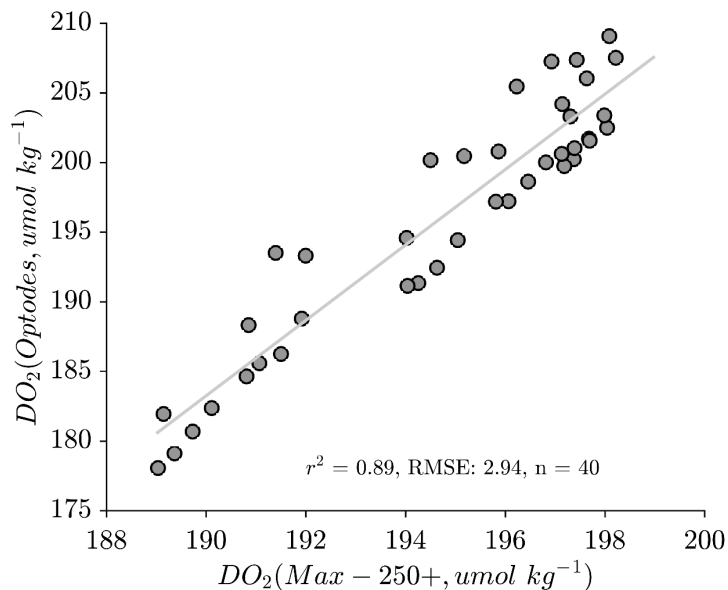


Figure S1: Linear regression of the Maxtec-250+ and optode sensor measurements during the early deployments at daily time scales. Each point represents the average of the early deployments at every 3-hour interval. This linear relationship was used to correct the MAX-250+ sensor: $3.11 (\pm 0.05) \times O_2 (\mu\text{mol/kg}) - 411 (\pm 11)$.

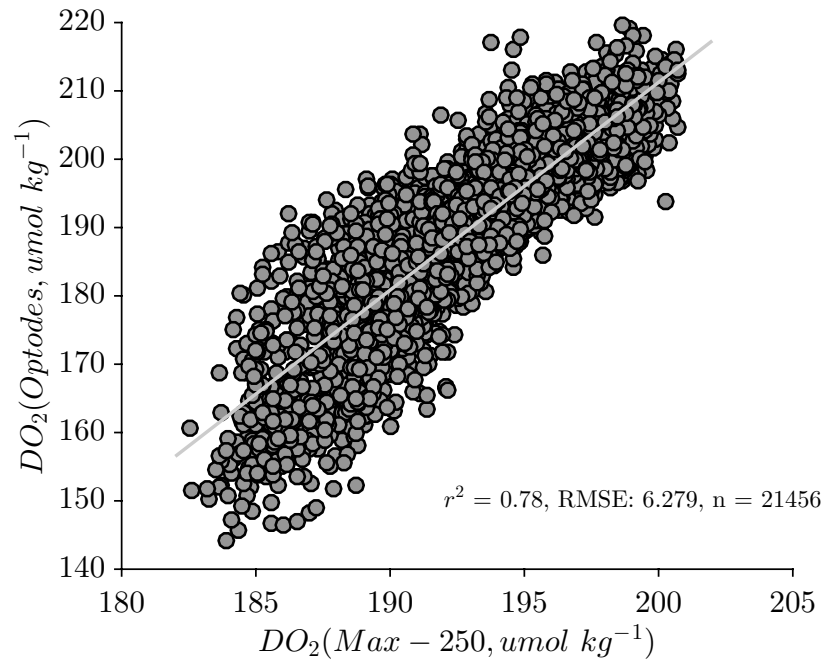


Figure S2: Linear regression of the Maxtec -250+ and Optode measurements during the first 300 days from 2009 to 2017 at every 3-hour interval. The linear relationship has a slope of 3.42 (± 0.002) and an intercept of - 471.3(± 0.35).

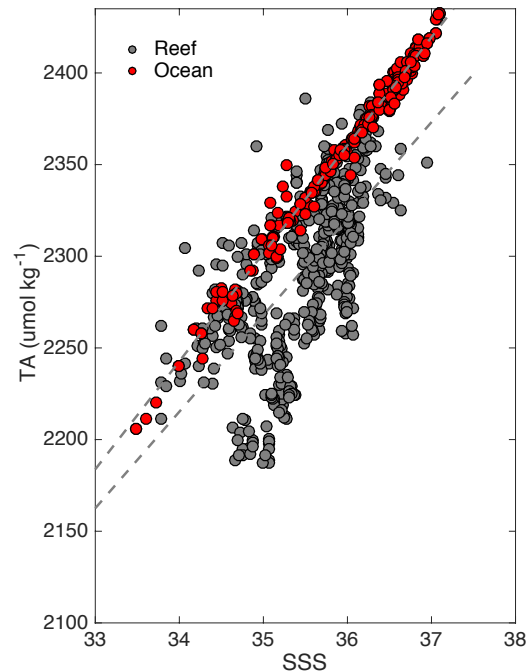


Figure S3: Linear relationship between TA and SSS for Enrique reef and open ocean water from the cruises around the Caribbean. The TA for Enrique forereef shows showed a moderate ($r^2 = 0.42$) but robust ($p < 0.0001$, $n = 547$) correlation to salinity with a slope of 52.29 (± 0.26) and an

intercept of 438 (± 9.45). The ocean end-member showed a strong ($r^2 = 0.99$) and robust ($p < 0.001$, $n = 237$) correlation with salinity with a slope of 58.9 (± 0.02) and offset of 237 (± 1).

References

Clayton, T. D., and Byrne, R. H.: Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Research Part I: Oceanographic Research Papers, 40(10), 2115-2129, 1993.

DOE: Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Seawater; version 2.0, edited by: Dickson, A. G. and Goyet, C., US Department of Energy CO2 Science Team Report, 1994.

Gran, G.: Determination of the equivalence point in potentiometric titrations of seawater with hydrochloric acid, Oceanol. Acta, 5, 209–218, 1952.

Dickson, A. G., Afghan, J. D., and Anderson, G. C.: Reference materials for oceanic CO2 analysis: a method for the certification of total alkalinity, Mar. Chem., 80, 185–197, 2003.

Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide to best practices for ocean CO2 measurements. Sidney, British Columbia, North Pacific Marine Science Organization, PICES Special Publication 3, 2007.